

New Side-Chain Liquid-Crystalline Ionomers. I. Synthesis and Characterization of a Homopolymer Derived from Ionic Mesogenic Groups

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ABSTRACT: Liquid-crystalline monomer cholesteryl 4-allyloxybenzoate (M_1), new ionic mesogenic monomer cholesteryl 4-allyloxy-3-(potassium sulfonate)benzoate (M_2), and corresponding polymer P_1 and ionomer P_2 were synthesized. The chemical structures of the monomers and homopolymer were confirmed with Fourier transform infrared and $^1\text{H-NMR}$ spectroscopy. The mesogenic properties were studied with differential scanning calorimetry, thermogravimetric analysis, polarizing optical microscopy, and X-ray diffraction measurements. The effect of the ionic units on the

phase behavior was examined. M_1 showed a cholesteric phase, and M_2 revealed a smectic A phase. P_1 and P_2 displayed smectic A phases. The experimental results demonstrated that the addition of ionic units to the mesogenic molecule not only affected the phase-transition temperature but also changed the mesogenic phase type. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2511–2516, 2004

Key words: ionomers; liquid-crystalline polymers; phase behavior; polysiloxanes

INTRODUCTION

Today, liquid-crystalline (LC) materials are directed toward the development of multifunctional structures. Such supermolecular systems include liquid-crystalline ionomers (LCIs). Both main-chain^{1–5} and side-chain^{6–12} LCIs have recently attracted considerable interest from those wishing to obtain new materials with desirable properties, such as mechanical, electrooptic, and magnetic properties. The reasons for having ionic units in these polymers are as follows: (1) ionic interactions can promote interchain interactions and improve the transverse mechanical properties for engineering materials, (2) ionic interactions similar to physical crosslinking effects can restrict the phase-separation process and result in microphases for the immiscible components as compatibilizers in polymer blend materials,^{13–17} and (3) ionic units may possess electric conductivity and magnetic activity and find applications in the fields of nanotechnology and magnetic data recording.^{18,19} Moreover, LCIs also play

important roles in understanding more complex biosystems.^{20–22}

In previous studies, many main-chain and side-chain LCIs have been prepared through the copolymerization of mesogenic monomers and nonmesogenic ionic monomers. However, to the best of our knowledge, very little research on LCIs derived from ionic mesogenic units has been reported. Therefore, it has been necessary to synthesize new side-chain LCIs to explore their potential applications. In this article, the synthesis of a new ionic mesogenic monomer and its corresponding LCI is described. The LC properties of the monomer and homopolymer have been characterized with differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), polarizing optical microscopy (POM), and X-ray diffraction (XRD) measurements.

EXPERIMENTAL

Materials

Poly(methyl hydrosiloxane) (PMHS; number-average molecular weight = 700–800) was purchased from Jilin Chemical Industry Co. (Jilin, China). Cholesterol was purchased from Henan Xiayi Medical Co. (Zhoukou, China). Toluene used in the hydrosilylation reaction was first refluxed over sodium and then distilled under nitrogen. All other solvents and reagents were purified by standard methods.

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Characterization

Fourier transform infrared (FTIR) spectra were measured on a Nicolet 510 FTIR spectrometer (Nicolet Instruments, Madison, WI). $^1\text{H-NMR}$ spectra (300 MHz) were recorded on a Varian WH-90PFT spectrometer (Varian Associates, Palo Alto, CA). The phase-transition temperatures and thermodynamic parameters were determined with a Netzsch DSC 204 (Netzsch, Germany) equipped with a liquid-nitrogen cooling system. The heating and cooling rates were $10^\circ\text{C}/\text{min}$. The thermal stability of the polymers under the atmosphere was measured with a Netzsch TGA 209C thermogravimetric analyzer. A Leica DMRX POM instrument (Leica, Germany) equipped with a Linkam THMSE-600 hot stage (Linkam, England) was used to observe phase-transition temperatures and analyze LC properties. XRD measurements were performed with nickel-filtered $\text{Cu K}\alpha$ ($\lambda = 0.1542$ nm) radiation with a DMAX-3A Rigaku powder diffractometer (Rigaku, Japan).

Synthesis of the monomers

The synthesis of the olefinic monomers is shown in Scheme 1. 4-Hydroxy-3-sulfobenzoic acid (**1**) was synthesized in our laboratory.

Cholesteryl 4-allyloxybenzoate (M_1)

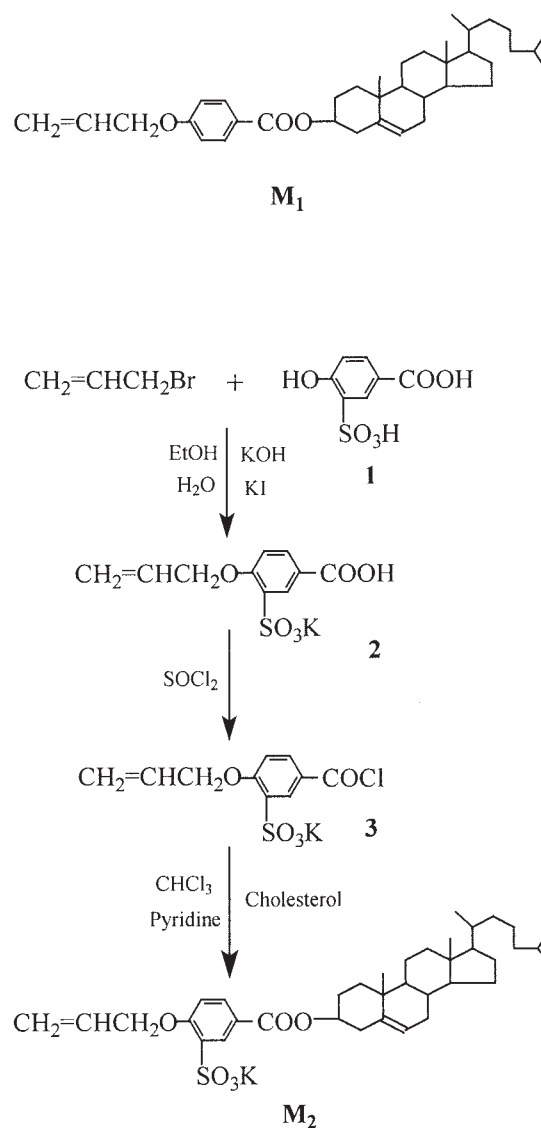
M_1 was prepared according to similar procedures previously reported.²³

Yield: 72%. mp: 107°C . IR (KBr): 3051 ($=\text{C-H}$), 2965, 2854 ($-\text{CH}_3$, $-\text{CH}_2-$), 1735 (C=O), 1634 (C=C), 1606, 1508 cm^{-1} (Ar-). $^1\text{H-NMR}$ (CDCl_3 , tetramethylsilane, δ , ppm): 0.67–2.03 (m, 43H, cholesteryl- H), 4.47 (t, 2H, $-\text{OCH}_2-$), 4.69–5.18 (m, 2H, $\text{CH}_2=\text{CH-}$), 5.36 (m, 1H, $=\text{CH-}$ in cholesteryl), 6.02 (m, 1H, $\text{CH}_2=\text{CH-}$), 6.92–7.98 (m, 4H, Ar-H).

4-allyloxy-3-(potassium sulfonate)benzoic acid (**2**)

First, **1** (44.0 g, 0.20 mol), potassium hydroxide (44.0 g, 0.79 mol), and a small amount of potassium iodide were dissolved in a solution of 100 mL of ethanol and 55 mL of water. Next, 3-bromopropene (24.3 g, 0.21 mol) was added dropwise to the solution. After stirring at 85°C for 16 h, the reaction mixture was poured into 100 mL of cold water and acidified with dilute hydrochloric acid. The resulting precipitate was filtered and washed with warm water. The crude product was recrystallized from water/ethanol (3:1). **2** was obtained as a solid.

Yield: 62%. mp: 218°C . IR (KBr): 3080 ($=\text{C-H}$), 2928, 2856 ($-\text{CH}_3$, $-\text{CH}_2-$), 2680, 2510 (COOH), 1698 (C=O), 1605, 1504 cm^{-1} (Ar-), 1270, 1230, 1209, 1121, $1050, 630\text{ cm}^{-1}$ (O=S=O). $^1\text{H-NMR}$ (dimethyl sulfox-



Scheme 1 Synthetic route of the mesogenic monomers.

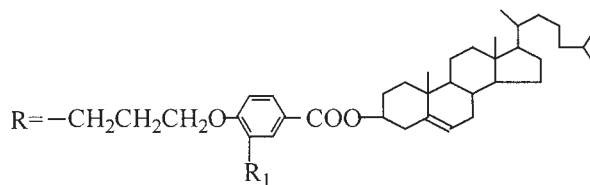
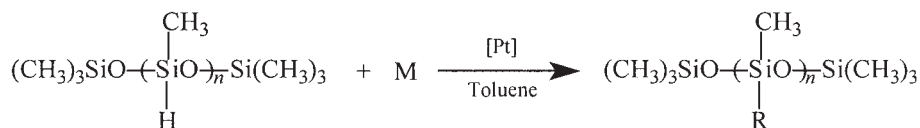
ide- d_6 , tetramethylsilane, δ , ppm): 4.83–5.07 (t, 2H, $-\text{OCH}_2-$), 5.67–5.78 (m, 2H, $\text{CH}_2=\text{CH-}$), 6.08–6.19 (m, 1H, $\text{CH}_2=\text{CH-}$), 7.23–8.32 (m, 3H, Ar-H), 8.57 (s, 1H, $-\text{COOH}$).

4-allyloxy-3-(potassium sulfonate)benzoyl chloride (**3**)

First, **2** (16.0 g, 0.056 mol) was reacted at 60°C with 30 mL of thionyl chloride and a few drops of *N,N*-dimethylformamide for 8 h, and then the excess thionyl chloride was removed under reduced pressure to give the corresponding acid chloride **3**. The yield was 62%.

Cholesteryl 4-allyloxy-3-(potassium sulfonate)benzoate (M_2)

3 (15.5 g, 0.05 mol) was dissolved in 20 mL of dry chloroform and added dropwise to a cold solution of



P₁, R₁ = -H

P₂, R₁ = -SO₃K

Scheme 2 Synthetic route of the polymers.

cholesterol (19.4 g, 0.05 mol) in 30 mL of pyridine and 30 mL of chloroform. The reaction mixture was refluxed for 30 h. The chloroform was removed, and the crude product was precipitated by the addition of water to the filtrate, acidified with dilute hydrochloric acid, and recrystallized from chloroform. A brown, solid powder was obtained.

Yield: 60%. mp: 139°C. IR (KBr): 2931, 2853 (—CH₃, —CH₂—), 1702 (C=O), 1604, 1505 (Ar—), 1268, 1216, 1121, 1026, 619 cm⁻¹ (O=S=O). ¹H-NMR (dimethyl sulfoxide-*d*₆, tetramethylsilane, δ, ppm): 0.82–2.81 (m, 43H, cholesteryl-*H*), 4.94–5.22 (t, 2H, —OCH₂—), 5.63–5.89 (m, 3H, CH₂=CH—, =CH— in cholesteryl), 6.09–6.20 (m, 1H, CH₂=CH—), 6.73–7.24 (m, 3H, Ar-*H*).

Synthesis of the polymer

The synthesis of the polymer is shown in Scheme 2. P₂ was synthesized as follows. Monomer M₂ (1.1 mol of Si—H) and PMHS were dissolved in freshly distilled toluene. The mixture was heated to 65°C under nitrogen and anhydrous conditions, and then 2 mL of a tetrahydrofuran solution of a hexachloroplatinate(IV) catalyst (5 mg/mL) was injected with a syringe. The progress of the hydrosilylation reaction, monitored from the Si—H stretch intensity, went to completion within 30 h, as indicated by FTIR. The solvent was removed, and the crude polymer was obtained by precipitation in toluene with excess methanol and then dried *in vacuo*.

IR (KBr): 2931, 2851 (—CH₃, —CH₂—), 1712 (C=O), 1612, 1510 (Ar—), 1300–1000 cm⁻¹ (Si—O—Si, S=O=S).

RESULTS AND DISCUSSION

Syntheses

The synthetic routes for the target monomer and polymer are shown in Schemes 1 and 2. M₂ was obtained through **3** reacted with cholesterol in chloroform and pyridine. IR spectra of M₂ showed characteristic bands of ester C=O at 1702 cm⁻¹, of aromatic C=C at 1605 and 1504 cm⁻¹, and of sulfonates at 1268, 1216, 1121, 1026, and 619 cm⁻¹. ¹H-NMR spectra of M₂ showed multiplets at 0.82–2.81, 5.63–6.20, and 6.73–7.24 ppm corresponding to methyl and methylene protons on cholesteryl units, olefinic protons, and aromatic protons, respectively.

The polymers were prepared through a hydrosilylation reaction between Si—H groups of PMHS and olefinic C=C of the mesogenic monomer in toluene with hexachloroplatinate(IV) as a catalyst at 65°C. IR spectra of the polymers showed the complete disappearance of the Si—H stretching band at 2166 cm⁻¹.

Thermal analysis

The thermal properties of the monomers and polymers were determined with DSC. The phase-transition temperatures and corresponding enthalpy changes, obtained during the second heating and first cooling cycles, are summarized in Tables I and II, respectively.

DSC heating thermograms of M₁ and M₂, respectively, showed two endothermic peaks, which represented melting transitions at 108.2 and 139.1°C, respectively, and LC–isotropic phase transitions at 223.7 and 238.3°C, respectively. On cooling scans, isotropi-

TABLE I
Phase-Transition Temperatures of the Monomers

| Monomer | Transition temperature ^{a,b} in °C (corresponding enthalpy changes in J/g): | | ΔT^c |
|----------------|---|---------|--------------|
| | Heating | Cooling | |
| M ₁ | K 108.2 (42.5) Ch 223.7 (1.6) I | | 115.5 |
| | I 215.7 (1.1) Ch 74.5 (31.3) K | | |
| M ₂ | K 139.1 (50.6) S _A 238.3 (2.9) I | | 99.2 |
| | I 229.5 (2.0) S _A 118.8 (44.3) K | | |

^a K = solid; Ch = cholesteric; S_A = smectic A; I = isotropic.

^b Peak temperatures were taken as the phase-transition temperature.

^c Mesophase temperature ranges on heating cycle.

c-LC phase transition appeared at 215.7 and 229.5°C, respectively, and crystallization temperatures appeared at 74.5 and 118.8°C, respectively. As Table I shows, the phase behavior of M₂ was strongly influenced by the presence of an additional sulfonate ionic unit in the mesogenic core. Compared with the melting temperature (T_m), isotropization temperature (T_i), and corresponding enthalpy changes (ΔH) of M₁, T_m , T_i , and ΔH of M₂ increased because the intermolecular interaction force improved when the ionic unit was added to the mesogenic core. Moreover, the mesophase temperature ranges decreased from 115.5 to 99.2°C because T_m increased more than T_i .

A glass transition at a low temperature and a mesophase-isotropic transition at a high temperature appeared on DSC curves of P₁. However, the DSC curve of P₂ only revealed a glass transition; no mesophase-isotropic phase transition was seen. However, POM observation results showed that P₂ displayed mesomorphic properties. In general, the glass-transition temperature (T_g) of side-chain LCs is influenced by the nature of the polymer backbone, the rigidity of the mesogenic units, the length of the flexible spacer, and the ionic unit. The ionic unit imposes additional constraints on the motion of chain segments because of physical crosslinking and aggregation and causes an increase in the T_g value. According to Table II, compared with T_g of P₁ with no ionic unit, the T_g value of P₂ increased by 41.0°C. Moreover, the ionic units of

the polymer also affected the mesogenic orientation order and T_i . Compared with that of P₁, the orientation order of P₂ was weakened, and T_i decreased by 66.3°C.

TGA results showed that the temperatures at which 5% weight loss occurred were greater than 300°C for P₁ and P₂; this shows that the synthesized polymers had higher thermal stability.

Texture analysis

The optical textures of the monomers and polymers were investigated via POM with cold and hot stages under a nitrogen atmosphere. POM showed that M₁ had an enantiotropic cholesteric phase and M₂ had a smectic A phase on heating and cooling cycles. When M₁ was heated to 106°C, the sample began to melt, the typical oily-streak texture gradually appeared, and the selective reflection color changed from red to blue with increasing temperature; the texture disappeared at 228°C. When the isotropic state was cooled to 219°C, the focal-conic texture appeared. When a mechanical force was superimposed on the sample, such as slight shearing, the melt caused macroscopic orientation of the cholesteric domains, and the focal-conic texture immediately transformed into the oily-streak texture, which is typical of cholesteric liquid crystals. When M₂ was heated to 136°C, a smectic fan-shaped texture appeared, and mesomorphic behavior disappeared at 239°C; the expected cholesteric phase did not appear because the interactions of the ionic unit and mesogenic unit hindered the formation of the helical supermolecular structure of the mesogens. This shows that the addition of the ionic unit to the mesogenic core not only influenced the LC phase-transition temperature but also changed the LC phase type and texture. Photomicrographs of M₁ and M₂ are shown in Figure 1(a-c).

Polymer P₁ showed a smectic broken fan-shaped texture, although the corresponding monomer showed a cholesteric phase, because the macromolecular chains hindered the formation of the helical supermolecular structure of the mesogens. Ionomer P₂ exhibited a smectic broken fan-shaped texture. Photomicrographs of P₁ and P₂ are shown in Figure 2(a,b).

TABLE II
DSC, TGA, and POM Results for the Polymers

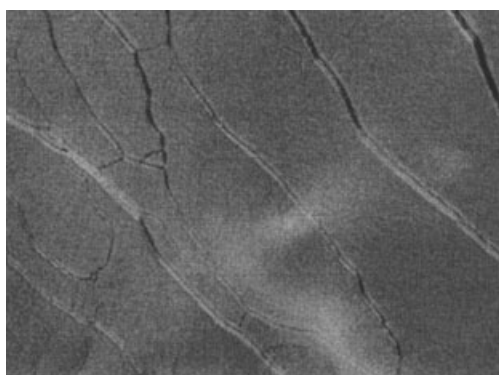
| Polymer | T_g (°C) | T_i (°C) | ΔH (J/g) | ΔT^b | T_d^c (°C) | LC phase |
|----------------|------------|------------------|------------------|--------------|--------------|----------------|
| P ₁ | 71.6 | 278.3 | 2.72 | 206.7 | 332.1 | S _A |
| P ₂ | 112.6 | 212 ^a | — | 99.4 | 319.5 | S _A |

S_A = smectic A.

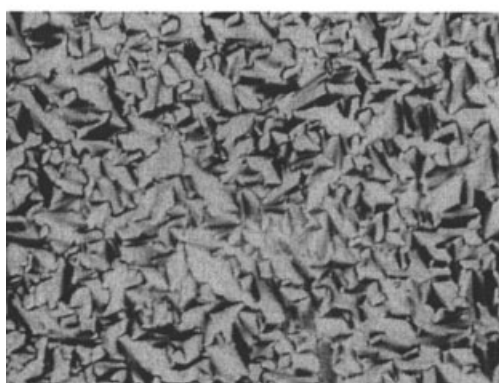
^a Observation with POM at 10°C/min.

^b Mesophase temperature ranges ($T_i - T_g$).

^c Temperature at which 5% weight loss occurred.



(a)



(b)



(c)

Figure 1 Optical textures of the monomers (200 \times): (a) oily-streak texture of M_1 on heating to 209 $^{\circ}\text{C}$, (b) focal-conic texture of M_1 on cooling to 212 $^{\circ}\text{C}$, and (c) fan-shaped texture of M_2 on heating to 182 $^{\circ}\text{C}$.

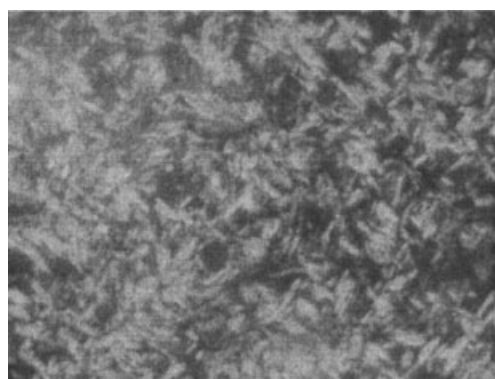
XRD analysis

XRD studies were carried out to obtain more detailed information on the LC phase structure. In general, a sharp and strong peak at a low angle ($1^{\circ} < 2\theta < 4^{\circ}$) in a small-angle X-ray scattering (SAXS) curve and a broad peak associated with lateral packing at $2\theta \approx 20^{\circ}$ in a wide-angle X-ray diffraction curve can be ob-

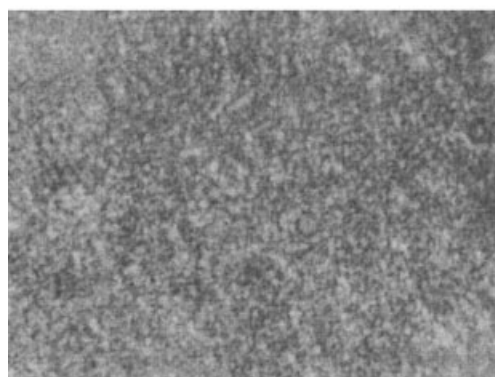
served for a smectic structure. For a nematic and cholesteric structure, no peak appears in a SAXS curve. Therefore, the LC phase structures can be confirmed according to the XRD characteristic peak, along with DSC and optical textures. For M_2 , P_1 , and P_2 , a strong small-angle reflection associated with the smectic layers was observed at 2θ values of 2.3, 2.8, and 2.5 $^{\circ}$, which corresponded to d -spacings of 39, 31, and 35 \AA .

CONCLUSIONS

In this study, we synthesized LC monomer M_1 , new ionic mesogenic monomer M_2 , and corresponding polymer P_1 and ionomer P_2 . The obtained polymers showed higher thermal stability. M_1 showed a cholesteric phase, and M_2 , P_1 , and P_2 had a smectic A phase. The addition of an ionic unit to the mesogenic molecule not only affected the phase-transition temperature but also changed the mesogenic phase type and texture.



(a)



(b)

Figure 2 Optical textures of the polymers (200 \times): (a) broken fan-shaped texture of P_1 at 226 $^{\circ}\text{C}$ and (b) broken fan-shaped texture of P_2 at 174 $^{\circ}\text{C}$.

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